Molecular and Macromolecular Photosensitizers in Photooxidation Reactions and Photovoltaic Cells

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SUMMARY: Based on low molecular and macromolecular phthalocyanines as light absorbing compounds different light driven reactions are shortly discussed. These processes include under irradiation with visible light energy transfer in photooxidation reactions and electron transfer in photosensibilisation cells or photovoltaic cells. Catalytic oxidation reactions are also mentioned to compare the different mechanisms of dark and light oxidations.

Introduction

Photosynthesis is the first fundamental process in nature using solar energy to oxidize water to oxygen and to reduce finally carbon dioxide to carbohydrates[1)]. Even that individual steps of the complex system are very efficient (quantum yiels >90 %), the conversion efficiency is only between 4 and 7 % (over the year less than 1 %). Some , steps of photosynthesis are:

- Collection of photons by light harvesting antennal systems and transport to the reaction center.
- Excitation of chlorophyll molecules and charge separation via the excited singlet state followed by electron or hole transport through redox chains.
- Formation of singlet oxygen from triplet oxygen via the excited triplet state of chlorophylls and then physical quenching by carotenoides.

Nature has been developed also several redox reactions proceeding without light via one-step, multi-electron transfer. Examples are catalyzed by cytochrome-oxidase or in the respiratory chain the reduction of oxygen to water accompanied by oxidation of other species.

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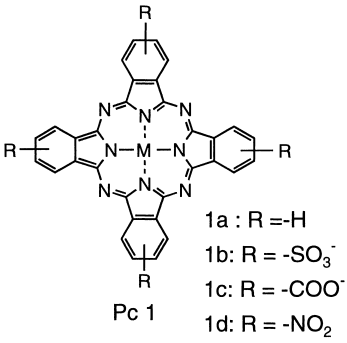
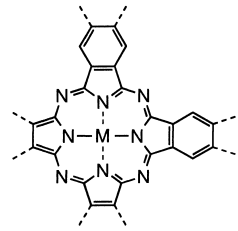
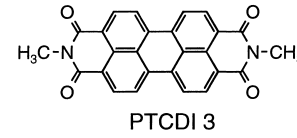
All these natural reactions of electron or energy transport are excellent examples how metal complexes in a macromolecular protein environment function are working. Therefore it is consequently to develop based on natural reactions artificial ones where macromolecular metal complexes are involved. This report concentrates on the following examples employing macromolecular metal complexes or multi-layered films of metal complexes:

- Catalytic oxidations of sulfur compounds and phenols for electron transfer[2].
- Photocatalytic oxidations as example of reactions running via energy transfer[3].
- Photosensibilisation cells as example of photo-induced electron transfer[4].
- Photovoltaic cells for photoinduced charge separation with molecular semiconductors in thin films[5].

As metal complexes low molecular weight and polymeric phthalocyanines **1**, **2** absorbing at λ~680 nm with ε~10^5 L mol^{-1} cm^{-1} and as carriers organic and inorganic macromolecules are used.







Catalytic oxidations of sulfur compounds

The MEROX (mercaptan oxidation) process is widely used in the treatment of petroleum distillates to convert thiols to disulfides and sulfide to sulfur (and also thiosulfate) by oxidation with air in aqueous alkaline solution in the presence of sulfonated Pcs **1b** (M= Co, V(O)) (Eqs. 1,2)[6]. Another reaction is the oxidation of phenols to quinones (Eq. 3).

$$4R\text{-}S^- + O_2 + 2H_2O \rightarrow 2R\text{-}S\text{-}S\text{-}R + 4HO^- \quad (1)$$

$$2H\text{-}S^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \quad (2)$$

$$C_6H_5O^- + O_2 \rightarrow C_6H_4O_2 + HO^- \quad (3)$$

Several CoPcs **1**, **2** on inorganic macromolecular carriers were prepared and employed as catalysts in aqueous alkaline solution for the oxidation of 2-mercaptoethanol. The mol mercaptan consumed per mol CoPc per min (turnover frequency, TOF) is a measure for the activity as shown in Tab. 1).

Compared to the commercially employed low molecular weight **1b** especially the polymeric **2** on charcoal and **1d** coordinatively bonded on silica exhibit higher activities[7,8].

Table 1. Turnover frequencies (TOF) of 2-mercaptoethanol oxidation at 298 K and pH 9. Molar ratio thiol/CoPc= 7000.

Sample	Loading ($\mu mol \cdot g^{-1}$)	TOF (min)	Ref.
Low mol. **1b**Co	-	853	7
1aCo dispersed on SiO_2	7.0	101	7
1aCo dispersed on charcoal	30.0	656	7
2Co dispersed on Al_2O_3	22.4	485	7
2Co dispersed on charcoal	5.0	1070	7
1cCo covalently bonded on SiO_2	1.4	849	8
1dCo coordinatively bonded on SiO_2	3.3	1981	8

Thermodynamically, the oxidation of thiolate to the disulfide proceeds for the reduction of O_2 via a two-step two-electron transfer ($O_2 + H^+ + 2e^- \rightarrow HO_2^-$; $HO_2^- + 3H^+ + 2e^{\ominus} \rightarrow 2H_2O$) or a one-step four electron transfer ($O_2 + 4H^+ + 4e^{\ominus} \rightarrow 2H_2O$) by help of the redox couples Co^{II}/Co^{I}, Co^{III}/Co^{II} in the macrocycle (proven by UV/Vis- and ESR-spectra)[8,9]: $E°(RSSR/RS^-)$= -0.20 V, $E°(O_2/HO_2^-)$= +0.39 V, $E°(O_2/H_2O)$= +0.71 V (all values at ~pH 9 vs NHE)[7,9]. In contrast, a one-electron transfer is not favorable: $E°(O_2/O_2^{\cdot-})$= -0.33 V, $E°(RS^{\cdot}/RS^-)$= +0.74 V. A detailed mechanism for the catalytic oxidation of sulfide was discussed recently[10].

Photocatalytic oxidations of sulfur compounds and phenols

Employing now water-soluble photosensitizer (PS) like **1b** with M=Zn or $Si(OH)_2$ more efficient photooxidations of the before mentioned substrates to the reaction products sulfonic acid, sulfate and - in the case of phenols - partially to carbon dioxide occur (Eqs. 4 - 6)[11-13].

$$2R\text{-}S^- + 3O_2 \rightarrow 2R\text{-}SO_3^- \quad (4)$$

$$H\text{-}S^- + 2O_2 + OH^- \rightarrow SO_4^{2-} + H_2O \quad (5)$$

$$C_6H_5O^- + 3.5O_2 + 4OH^- \rightarrow CO_3^{2-} + HCOO^- + {}^-OOC\text{-}CH{=}CH\text{-}COO^- + 3H_2O \quad (6)$$

The Zn- and Si-phthalocyanines **1b** exhibit no activity in the dark, which means they show no catalytic effect. But under irradiation a high photoactivity is observed exemplarily. Fig. 1a compares the photocatalytic activity of the low molecular weight **1b** (M=$Si(OH)_2$) with this PS ionically bonded to the cation exchanger Amberlite (TiO_2 for comparison also shown). The polymer bonded PS is highly active and also stable over several runs which can be seen from Fig. 1b.

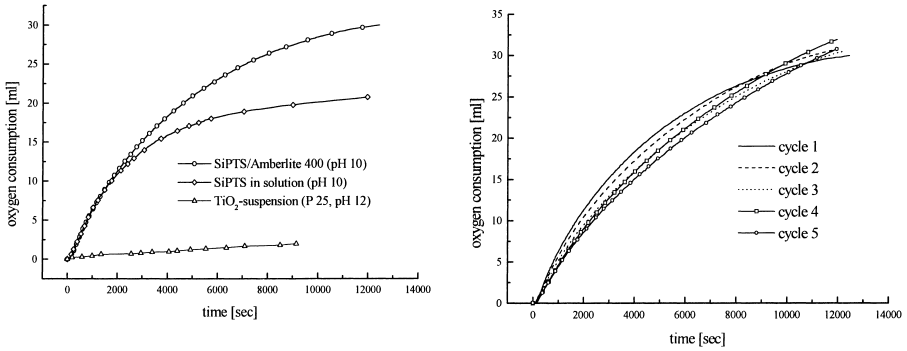


Fig. 1: Photooxidation of 0.358 mmol phenol in 50 ml aqueous alkaline solution by irradiation with a slide projector of 180 mW cm^{-2}. Left: Comparison of the activity of different photocatalyst: 0.25 µmol **1b** (M= $Si(OH)_2$), 10 µmol **1b** (M=$Si(OH)_2$) on Amberlite, 160 mg TiO_2. Right: 0.358 mmol phenol added 5 times to a solution containing 10 µmol **1a** (M=$Si(OH)_2$).

Experiments were also conducted under solar radiation using a simple satellite receiver bowl carefully coated with an aluminium foil. Under a light intensity of ~1000 mW cm^{-2} the activity is much higher compared to irradiation with a slide projector in the photooxidation of

for example 2-chlorophenol: Maximum O_2 consumption under solar radiation after ~1000 sec, with a slide projector after ~2000 sec using **1b** (M= Al(OH)) as PS[3)].

The mechanism of the photocatalytic oxidations are quite different compared to the catalytic oxidations. The main pathway uses after excitation to the singlet state ($^1PS^*$) the intersystem crossing (ISC) to the excited triplet state ($^3PS^*$). Then the spin allowed energy transfer from $^3PS^*$ to triplet oxygen ($^3O_2$, $^3\Sigma_g^-$) results in singlet oxygen ($^1O_2$, $^1\Delta_g$) in quantum yields of ~50 %[14)] followed by oxidation of the substrate (Sub) (Eq. 7 -9). Due to the triplet energy of MPcs with ~1.1 eV and the energy difference between triplet and singlet oxygen of 0.98 eV energy transfer is possible which was also shown by quenching experiments[11)].

$$PS \xrightarrow{h\nu} {}^1PS^* \xrightarrow{ISC} {}^3PS^* \quad (7)$$

$$^3PS + {}^1O_2 \rightarrow PS + {}^1O_2 \quad (8)$$

$$^1O_2 + Sub \rightarrow \text{oxidized Sub} \quad (9)$$

Photosensibilisation cells

Nanocrystalline solar cells consisting of an electrode of a photosensitizer adsorbed on TiO_2 dipped in a redox electrolyte in the presence of a counter electrode have attracted significant attention as low-cost alternative to conventional solid state photovoltaic cells (Si, GaAs etc.)[15,16)]. In order to improve the activity of such cells in the near IR-region, phthalocyanines were employed in the cell configuration of a size 0.44 cm^2: [4)]

$$SnO_2/TiO_2\text{-MPc}/I_3^-,I^- \text{ in propylene carbonate/Pt on } SnO_2$$

Under irradiation with full AM 1.5 solar light differently substituted phthalocyanines were tested. Exemplarily **1c** (M= Zn) exhibit the following characteristic data: open-circuit voltage (V_{OC} 490 mV, short-circuit photocurrent (I_{SC}) 5 mA cm^{-2}, fill factor (FF) 0.49, overall conversion efficiency (η) 1 % and a very high incident photon-to-current conversion efficiency of 43 % at 700 nm.

Mechanistically now, the excited singlet state $^1PS^*$ of ZnPc (E°~ -0.9 V) and not the excited triplet state (E~ -0.2 V vs NHE) is quenched oxidatively by TiO_2 (conduction band at -0.5 V vs NHE), and the electron is transported via the counter electrode and the redox electrolyte back to the oxidized PS (Eq. 10 - 12)[4)].

$$PS + h\nu \rightarrow {}^1PS^* \rightarrow PS^{\bullet+} + e^{\ominus} \text{ (to } TiO_2) \quad (10)$$

$$e^{\ominus} + 0.5\ I_2 \rightarrow I^- \quad (11) \qquad I^- + PS^{\bullet+} \rightarrow 0.5\ I_2 + PS \quad (12)$$

Photovoltaic cells based on molecular organic semiconductors

Thin films of phthalocyanines **1** (Pc) and 3,4,9,10-perylenetetracarboxylic acid diimides **3** (PTCDI) are characterized as *van-der-Waals* bonded molecular organic semiconductor[5]. Pcs exhibit p-type and PTCDIs n-type conductivity as for example determined by the Seebeck coefficient, junction behavior in Schottky-cells or in photoelectrochemical experiments[5]. Photovoltaic cells of p/n-junction type of the following configuration were prepared and measured in air under illumination of 100 mW cm^{-2} from the ITO side[17]:

ITO/**3** (10-100 nm)/**1a** (M= Zn) (10-100 nm)/Au (10-30 nm)

Exemplarily presented results in Tab. 2 show that overall conversion efficiencies η of < 0.5 % can be obtained under high light intensity. I_{SC} in the order of few mA cm^{-2} are one order of magnitude lower compared to Si-photovoltaic cells. Also the FF is only 50 % compared to the inorganic cells whereas V_{OC} is approaching them. The increase of μ with decreasing light intensity shows that charge limited currents occur in these high ohmic materials which lead to recombination of excitons.

Table 2. Characteristic values of some exemplarily selected organic photovoltaic cells (irradiation with 100 mW cm^{-2} under air).

n-Conductor	p-Conductor	I_{SC} (mA cm^{-2})[2]	U_{OC} (mV)	FF	η (%)
PTCDI (75 nm)	CuPc (75 nm)	1.92	415	0.41	0.33
PTCDI (50 nm)	H_2Pc (50 nm)	2.57	550	0.30	0.56
PTCDI (75 nm)	ZnPc (75 nm)	2.38	345	0.34	0.28
PTCDI (75 nm)	ZnPc (75 nm)	0.56	305	0.36	0.62[a]
PTCDI (75 nm)	ZnPc (75 nm)	0.14	255	0.42	1.51[b]

[a] Light intensity 10 mW cm^{-2}. [b] Light intensity 1 mW cm^{-2}.

Under irradiation (bandgap Pc~1.7 eV, PTCDI~2.2 eV) excitons are formed which are separated in the small depletion region (~20 - 30 nm) resulting in electron flow to the PTCDI and hole flow to the Pc. One main problem is the recombination of excitons in 50-100 nm thick films. This thickness is necessary to absorb enough light (extinction coefficients of the molecular semiconductors ~10^5 cm^{-1}). It was shown that in n/p-junction devices of 10 nm films the quantum yield of the photocurrent increases up to 75 % which means that nearly every absorbed photon produces separated charge carriers[17]. But due to low absorptions of these thin film the I_{SC} decreases with decreasing layer thickness.

Fig. 2 shows the absolute positions of energy levels of the materials for the described cell configuration before contact. The p-conducting ZnPc is doped in air by oxygen: ZnPc + O_2 ⇄ $ZnPc^{\delta+} + O_2^{\delta-}$ ⇄ $ZnPc^{+} + O_2^{-}$. Important is the difference in the position of the Fermi levels (E_F). Therefore after contact with equilibrium of E_F down-hill bending of the energy levels of the ZnPc and up-hill bending of the PTCDI occurs. Under irradiation now, holes flow to the ZnPc and electrons to the PTCDI.

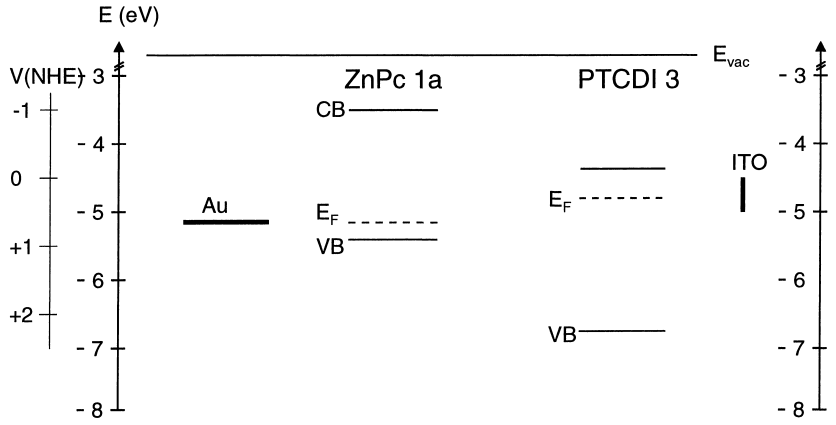


Fig. 2:Energy band diagramm of an ITO/PTCDI/ZnPc/Au cell. VB valence band, CB conduction band, E_F Fermi level.

Conclusion

The shortly discussed examples clearly demonstrated that under irradiation different processes of energy transfer (photooxidation) and electron transfer (photosensibilisation) and electron transfer (photosensibilisation cells, photovoltaic cells) occur. Exemplarily, reactions of catalytic electron transfer were included to show that totally different mechanisms exist under dark or irradiation. In principle, the activities in the mentioned examples are high and hopefully for a further increase in future work.

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